

Environmentally friendly epoxidation of olefins under phase-transfer catalysis conditions with hydrogen peroxide

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Abstract

Several catalysis systems, $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / \text{Q}^+ \text{A}^- / \text{H}_3\text{PO}_4 / \text{H}_2\text{SO}_4 / \text{solvent}$ ($\text{Q}^+ \text{A}^- = \text{Arquad 2HT}^\circledast$, $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{Cl}^-$; $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{HSO}_4^-$, $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^-$; solvent: CHCl_3 or toluene) were used to selectively and efficiently convert olefins to their corresponding epoxides at room temperature. With cyclooctene and using Arquad 2HT[®] as the phase-transfer agent, there is a synergy when both phosphate and sulfate anions are present in the reaction medium compared with systems using either one or the other. The importance of the tungsten(VI) source is, as found previously, underlined by the strong activity increase when $\text{WO}_3 \cdot \text{H}_2\text{O}$ is used instead of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, even at room temperature. The influence of the phase-transfer agent $\text{Q}^+ \text{A}^-$ has been evaluated for the system $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / \text{Q}^+ \text{A}^- / \text{toluene}$. With $\text{Q}^+ \text{A}^-$ ($\text{Q}^+ = [\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+$ and $\text{A}^- = \text{Cl}^-$, HSO_4^- , and H_2PO_4^-), the best results for the conversion of cyclooctene at room temperature are obtained with $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^-$. ³¹P NMR experiments show the transfer in the organic phase of the $[\text{PO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]^{3-}$ and $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]^{2-}$ complexes with H_3PO_4 and H_2PO_4^- , whereas only $[\text{PO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]^{3-}$ can be identified with the addition of $\text{H}_3\text{PO}_4 / \text{HSO}_4^-$ or $\text{H}_2\text{PO}_4^- / \text{H}_2\text{SO}_4$. Moreover, acid-sensitive epoxides can be prepared using buffers generated by the addition of sodium hydrogenocarbonate or, preferably, disodium hydrogenophosphate, leading to high selectivities toward the corresponding epoxides. The data show that disodium hydrogenophosphate gives the best results even if the reaction time has to be increased to obtain high conversions. The $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} / [\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^- / \text{toluene}$ catalysis system can be reused in 5 consecutive runs with no loss in activity.

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1. Introduction

From an ecological standpoint, the exclusion of pollutants from an unselective preparation method is always preferable to subsequent treatment. In this context, the goal of modern organic synthesis is to develop efficient catalytic methods that can produce compounds with atom economy and environmental advantages. Considering oxidation reactions with oxygen

donors, one preferred method involves using technology based on catalytic oxygen transfer from *clean* oxygen donors, such as hydrogen peroxide (and also on novel and cleaner methods for its preparation in the long term). This choice is motivated by its ease of handling and high active oxygen content, as well as the fact that water is the sole byproduct [1–5]. In the area of oxidation by H_2O_2 , the selective epoxidation of alkenes remains a principal objective. Epoxides are valuable and reactive intermediates, owing to the large range of reactions that they undergo in organic and pharmaceutical chemistry. The reaction products find applications as plasticizers, detergents, surfactants, surface-coating agents, bioactive substances, and others [6,7].

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In 1959, Payne and Williams proposed for the first time the epoxidation of α,β -unsaturated acids using sodium tungstate as a precatalyst with H_2O_2 [8]. Given that two-phase mixtures are obtained with aqueous H_2O_2 and olefinic substrates, two-phase or phase-transfer catalysis systems have been developed. The reactions can be carried out under mild conditions, and high reaction rates are generally observed [9–14]. Since then, numerous two-phase epoxidation processes using H_2O_2 as the primary oxidant and tungsten-based oxoperoxo anions with an onium salt have been claimed to be as active and selective as $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{organic solvent}$ catalytic systems [14]. Epoxidation of olefin via phase-transfer catalysis (PTC) was investigated under Venturello's conditions [15] ($\text{Na}_2\text{WO}_4/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{H}_3\text{PO}_4/\text{organic solvent}/\text{onium chloride}/70^\circ\text{C}$) and Ishii's conditions [16,17] ($\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot\text{aq}/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{organic solvent}/\text{onium salt}/60^\circ\text{C}$). It was demonstrated [14,18,19] that the two catalyst systems involve common oxoperoxo anions, despite the fact that each group patented its particular set of catalyst precursors as novel chemistry (for a recent review see [20]).

A thorough study of these catalyst systems was conducted to synthesize and characterize several tungsten(VI) and/or molybdenum(VI) complexes with different assembling anions, such as $[\text{PO}_4]^{3-}$ [21], $[\text{HPO}_4]^{2-}$ [18], $[\text{AsO}_4]^{3-}$ [22], $[\text{HAsO}_4]^{2-}$ and $[\text{CH}_3\text{AsO}_3]^{2-}$ [23], $[\text{SO}_4]^{2-}$ [24], $[\text{R}_2\text{SiO}_2]^{2-}$, $[\text{Ph}_3\text{SiO}]^-$ and $[\{\text{Ph}_2\text{SiO}\}_2(\mu\text{-O})]^{2-}$ [25–27]. It was also shown that the transfer of active oxygen of these complexes to olefinic substrates depends on the amount and nature of the phase-transfer agent and on the assembling anion. The sulfato group was found to have a promoting effect for both tungsten and molybdenum complexes with the $\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$ moiety ($\text{M} = \text{Mo}, \text{W}$) [24]. At room temperature, under stoichiometric conditions, the active species, mainly $[\text{SO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$, denoted as SW_2 (see Fig. 1a), can be regenerated only in acidic

media ($\text{H}_2\text{O}_2\text{-H}_2\text{O-H}_2\text{SO}_4$); otherwise a poorly active trinuclear anion is formed.

More recently, a catalytic system comprising sodium tungstate dihydrate, (α -aminomethyl)phosphonic acid (AMPA), and methyltri-*n*-octylammonium hydrogenosulfate, Q^+HSO_4^- was described for the epoxidation of olefins using aqueous 30 wt% hydrogen peroxide as a primary oxidant at $70\text{--}90^\circ\text{C}$ [28]. Reaction proceeds in high yield without solvent or, alternatively, with toluene, under entirely halide-free conditions. High yields for the epoxidation of cyclooctene and of various substrates were reported, but the procedure was performed at approximately 90°C . Note that (i) AMPA and the lipophilic ammonium hydrogenosulfate Q^+HSO_4^- are crucial for the high reactivity as is the pH of the aqueous phase ($\text{pH} \leq 3$); (ii) AMPA decomposes under the reaction conditions to form mainly H_3PO_4 and/or $[\text{HPO}_4]^{2-}$; (iii) the P(V):W(VI) ratio corresponds to that for the synthesis of $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$, denoted PW_2 and a deficiency of Q^+ is beneficial [$\text{Q}^+:\text{P(V)} \approx 1$ instead of 2 for PW_2 and $\text{Q}^+/\text{W(VI)} \approx 0.5$] as reported previously [29]; and (iv) the activity is raised by increasing the temperature (90°C), but this is not a good option for epoxidation due to the hydrolytic ring-opening of epoxides. In Noyori's proposal, the active species (and/or aggregation state) are unknown. Dawson-type heteropolyoxometalates with $[\text{R}_4\text{N}]_4[\text{S}_2\text{W}_{18}\text{O}_{62}]/\text{CH}_3\text{CN}/\text{H}_2\text{O}_2\text{-H}_2\text{O}$ systems also have been used to oxidize cyclohexene to adipic acid in high yield [30]. The active species (i.e., sulfato-based complexes, possibly SW_2) have not been identified.

Epoxidation of olefins such as cyclohexene with hydrogen peroxide in a two-phase medium was also carried out under PTC conditions using a quaternary ammonium heteropolyoxotungstate, $\text{Q}_3[\text{PW}_4\text{O}_{16}]$ which is degraded into several oxoperoxophosphato species in the reaction [31]. Similarly, epoxida-

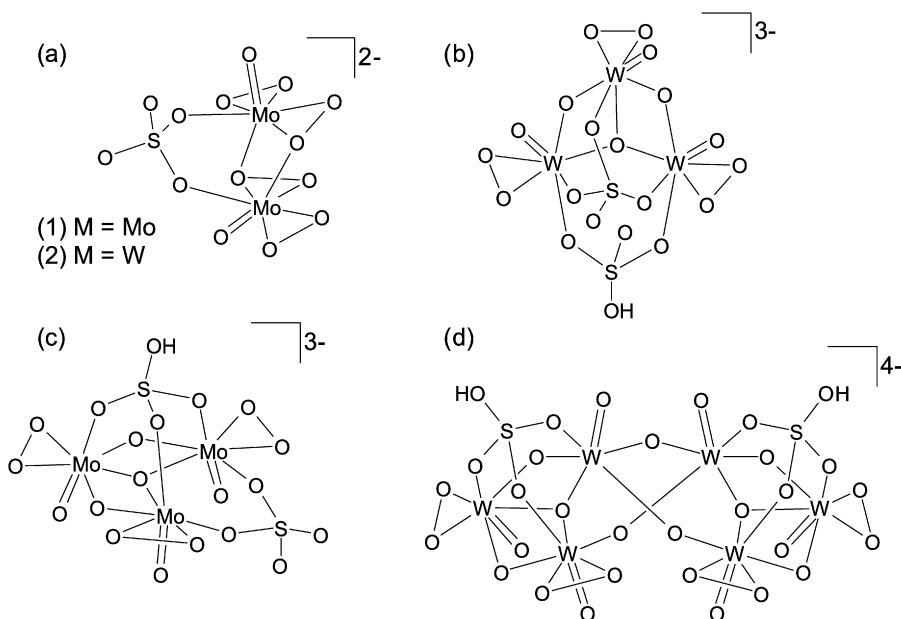


Fig. 1. Representation of the anions: $[(\text{SO}_4)\{\text{Mo}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ (a), $[(\text{HSO}_4)(\text{SO}_4)\{\text{W}_3\text{O}_6(\text{O}_2)_3\}]^{3-}$ (b), $[\text{H}(\text{SO}_4)_2\{\text{Mo}_2\text{O}_2(\text{O}_2)_3\}]^{3-}$ (c) and $[\{\text{H}(\text{SO}_4)\text{-W}_3\text{O}_7(\text{O}_2)_2\}_2\text{O}]^{4-}$ (d). Crystal structures for species (a1) [24], (b) [24], (c) [37] and (d) [38] have been solved, while for the tungsten dinuclear compound (a2), structural identification is suggested on the basis of cell parameters, space group and similar IR and Raman spectra obtained for (a1) and (a2) [24].

tion of dicyclopentadiene under PTC conditions was investigated in a two-phase system comprising an acidic solution and an organic solvent. The reaction is enhanced by a quaternary ammonium salt when hydrogen peroxide is used as the oxidizing agent, with sodium tungstate and phosphoric acid as the co-catalysts [32,33].

In the present work, we examine the potential of the simple, chloride-free catalysis system $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / \text{Q}^+ \text{A}^- / \text{olefin} / \text{solvent}$ at 20–60 °C (where Q^+ is a quaternary ammonium cation and A^- are different anions) with several sulfate and/or phosphate sources. We show for the first time that the direct addition of both phosphate and sulfate anions to the reaction medium leads to enhanced activity compared with systems with either alone. The influence of the $\text{Q}^+ \text{A}^-$ onium salt is also discussed. The partition of the active species between the organic and aqueous phases is characterized by ^{31}P NMR investigations.

2. Experimental

All solvents (CHCl_3 , toluene, acetone) were commercially available and used without further purification. Tungstic acid, $\text{WO}_3 \cdot \text{H}_2\text{O}$, was obtained from Eurotungstène. 30 wt% aqueous hydrogen peroxide (without phosphate) was bought from VWR. Sulfuric and orthophosphoric acids were pure analytical reagents diluted with distilled water. Trimethylphosphate, $(\text{CH}_3\text{O})_3\text{PO}$ (97% pure) and tri-*n*-octylamine (98% pure) were purchased from Aldrich. Cyclooctene and 1-octene (obtained from Fluka) were >98% pure by GC and ^1H NMR analysis. (*R*)-(+)-limonene (98% pure), 7-methyl-3-methylene-1,6-octadiene (β -myrcene, 90% pure), 3,7,7-trimethylbicyclo[4.1.0]hept-3-ene (δ^3 -carene, 90% pure), and (*S*)-(+)-3,7-dimethyl-1,6-octadiene [(+)- β -citronellene, >98%, sum of enantiomers] were purchased from Aldrich. Arquad 2HT® is a mixture of two quaternary ammonium chlorides, $[\{(n\text{-C}_{18}\text{H}_{37})_{75}\% + (n\text{-C}_{16}\text{H}_{33})_{25}\}\text{N}(\text{CH}_3)_2\text{Cl}^-]$, marketed by Akzo. It was used after being washed three times with acetone, followed by air drying. Aliquat® 336, $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{Cl}^-$, was obtained from Aldrich.

Elemental analyses were carried out at the Service Central d'Analyses, CNRS, Lyon.

2.1. Preparation of methyltri-*n*-octylammonium hydrogensulfate and methyltri-*n*-octylammonium dihydrogenophosphate phase-transfer agents

$[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-$ was prepared following an adaptation of the procedure described for $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{HSO}_4^-$ [34]. First, 20 mL of toluene and 17.7 g (50.0 mmol) of tri-*n*-octylamine were mixed in a round-bottomed flask. Under moderate stirring, 7.21 g of trimethylphosphate (51.5 mmol) were added in portions at room temperature. The mixture was heated to 140 °C for 23 h, after which 2.0 mL of water were added to the resulting pale-yellow solution. The mixture was then heated at 90 °C for 26 h. After cooling, aqueous 13.6 wt% H_3PO_4 (20.0 mL) was added, and the resulting white two-phase mixture was stirred at room temperature for

15 h. Finally, the solvents were evaporated to give 22.6 g of $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-$ (yield, 97%).

2.2. Synthesis of the salt of the Arquad® cation: $\text{Q}_2[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]$ denoted $\text{Q}_2[\text{PW}_2]$

The complex was synthesized according to the previously published procedure [18]. To a 30 wt% aqueous solution of hydrogen peroxide (7 mL, 69 mmol), was added $\text{WO}_3 \cdot \text{H}_2\text{O}$ (2.5 g, 10 mmol). After 60 min of stirring at 60 °C, cooling to room temperature, and centrifugation (15 min at 2000 rpm), the unreacted solid was separated out. Then 6 M H_3PO_4 (0.85 mL, 5.1 mmol) was added to the supernatant. A solution of Arquad 2HT® (3.3 mmol) in 20 mL of CHCl_3 was added dropwise to the clear solution. After 15 min of gentle stirring, the two phases were separated. The organic phase was dried with MgSO_4 and the solvent removed using a rotary evaporator. ^{31}P NMR (CDCl_3): $\delta = +0.5$ ppm (broad signal).

2.3. Catalysis test

2.3.1. In-situ generation of oxoperoxo tungsten species

First, 30 wt% hydrogen peroxide (1.2 mL; 10.3 mmol) was mixed with $\text{WO}_3 \cdot \text{H}_2\text{O}$ (0.13 mmol) along with 1 mL of water at room temperature. After 10 min of stirring (necessary for the precursor to react completely), the desired amount of phosphoric and/or sulfuric acid was added (see Tables 1 and 2). The solution was then transferred to a Schlenk tube containing a chloroform or toluene solution (5 mL) of the phase-transfer agent (see Tables 1–5). After the two phases were stirred for 2 min, 7.7 mmol of substrate was added. The mixture was then stirred at the desired temperature (usually 21 °C).

The reuse of the $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / [\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^- / \text{alkene} / \text{toluene}$ catalytic system was evaluated as follows. First, 10.3 mmol of aqueous 30 wt% hydrogen peroxide, then 7.7 mmol of substrate, were added to the two-phase mixture. The course of the reaction was monitored by analyzing the organic phase by gas chromatography on a Delsi 30 apparatus equipped with a capillary column (OV 1701, 0.25 mm \times 50 m), using helium as carrier gas (40 $\text{cm}^3 \text{min}^{-1}$) and a flame ionization detector (hydrogen flow: 20 $\text{cm}^3 \text{min}^{-1}$; air flow: 300 $\text{cm}^3 \text{min}^{-1}$) linked to a Delsi Enica 10 electronic integrator; initial column temperature of 70 °C, a final column temperature of 200 °C, an injection temperature of 170 °C, a detector temperature of 170 °C, and a heating rate of 3 °C min^{-1} . Substrate conversion and product selectivity were determined using hydrocarbons as internal standards. Cumulative errors are believed to be 3–6% or less in most cases. Identification of epoxides was based on GC retention times and on mass spectral data (GC–MS [18,19]). Product identification of oxides was confirmed by subsequent ^{13}C NMR spectroscopy.

2.3.2. Catalysis tests with the salt of the Arquad® cation: $\text{Q}_2[\text{PW}_2]$

Approximately 0.05 mmol of the complex salt was dissolved in a Schlenk tube containing 5 mL of CHCl_3 . Then water (1 mL) and 30 wt% hydrogen peroxide (1.2 mL; 10.3 mmol)

Table 1

Epoxidation of cyclooctene at 21 °C with aqueous 30 wt% hydrogen peroxide using Arquad 2HT® as phase-transfer catalyst or the salt of the Arquad cation for the dinuclear polyoxoperoxometalate compound: Q₂[PW₂]

Entry ^a	Solvent	Precursor (mmol)	H ₃ PO ₄ (mmol)	H ₂ SO ₄ (mmol)	Time (h)	Conversion ^b (%)	Selectivity ^b (yield) (%)
1	CHCl ₃	WO ₃ ·H ₂ O (0.13)	0	0	73	32	78 (25)
2	CHCl ₃	WO ₃ ·H ₂ O (0.13)	0	0.85	7	97	100 (97)
3	CHCl ₃	WO ₃ ·H ₂ O (0.13)	0	3.4	19	96	100 (96)
4	CHCl ₃	WO ₃ ·H ₂ O (0.13)	0.036	0	1	72	100 (72)
					2	97	100 (97)
5	Toluene	WO ₃ ·H ₂ O (0.13)	0.036	0	1	55	100 (55)
6	CHCl ₃	WO ₃ ·H ₂ O (0.13)	0.036	3.4	0.5	97	100 (97)
7	CHCl ₃	WO ₃ ·H ₂ O (0.13)	0.036	1.7	1	99	100 (99)
8	CHCl ₃	Q ₂ [PW ₂] (0.05)	0	0	2	57	100 (57)
9	CHCl ₃	Q ₂ [PW ₂] (0.05)	0	3.4	2	99	100 (99)
10	CHCl ₃	Q ₂ [PW ₂] (0.05)	0	6.8	2	97	100 (97)
11	Toluene	WO ₃ ·H ₂ O (0.13)	0.036	1.7	2	98	100 (98)

^a Reaction under PTC conditions 21 °C: phase-transfer agent (Q⁺Cl⁻) = Arquad 2HT® (see Section 2) (0.0975 mmol), 30 wt% H₂O₂ (10.3 mmol), H₂O (1 mL), solvent (5 mL), olefin (7.7 mmol), Q₂[PW₂]: Q₂[HPO₄{W₂O₂(μ-O₂)₂(O₂)₂}], pH 1.5–3.5 (initial to final values of the aqueous phase).

^b Determined by GC analysis.

Table 2

Epoxidation of cyclooctene using methyltri-*n*-octylammonium hydrogenosulfate as phase-transfer catalyst^a

Entry	H ₃ PO ₄ ^b (mmol)	H ₂ SO ₄ (mmol)	Solvent	Reaction time (h)	Conversion ^c (%)	Selectivity ^c (%)	Yield ^c (%)
1	0	0	CHCl ₃	0.5	14	100	14
				1	25	100	25
				4.5	72	100	72
				6	82	100	82
				14	99	100	99
2	0.036	0	CHCl ₃	0.5	47	100	47
				1	99	100	99
3	0.036	0	Toluene	1	94	100	94
4	0.036	1.7	CHCl ₃	1	99	100	99
5	0.036	1.7	Toluene	2	90	100	90

^a Reaction under PTC conditions at 21 °C: WO₃·H₂O (0.13 mmol), 30 wt% H₂O₂ (10.3 mmol), H₂O (1 mL), solvent (5 mL), olefin (7.7 mmol), [CH₃(*n*-C₈H₁₇)₃N]⁺HSO₄⁻ (0.0975 mmol).

^b Phosphoric acid was added after mixing the organic and aqueous phases.

^c Determined by GC analysis.

were added, and the two-phase mixture was stirred for 2 min before the substrate was added. The workup was as described in the previous section.

2.4. NMR measurements

³¹P NMR spectra were recorded in 5-mm-o.d. passivated tubes (to minimize H₂O₂ decomposition) on a Bruker AC 300 apparatus operating at 121.4 MHz in the Fourier transform mode. Aqueous peroxide solutions were obtained by reacting tungstic acid (1 mmol) in 2 ml of 30 wt% hydrogen peroxide. After complete reaction (nearly 10 min), 1 M H₃PO₄ (0.25 ml; 0.25 mmol) was added with stirring. The colorless solution was transferred into a tube containing the desired phase-transfer agent in CHCl₃ solution. The mixture was then stirred for 30 min at room temperature, and the organic phase was analyzed by ³¹P NMR. Chemical shifts are referenced to external 85% H₃PO₄ and are not corrected for bulk magnetic susceptibility. ¹H NMR (300 MHz) and ¹³C NMR (50 MHz)

spectra were recorded on Bruker AC300 and 200 spectrometers at 25 °C using TMS as reference.

3. Results and discussion

3.1. Preliminary tests with cyclooctene

Due to the deleterious effect of Na⁺ ions and of Na⁺Cl⁻, which significantly modify the equilibria of anionic species between organic and aqueous phases in PTC systems, WO₃·H₂O, the oldest of the known precatalyst, is, as found previously, the preferred tungsten precursor [14,18–20,22–27,29,35]. It readily reacts with aqueous H₂O₂ at room temperature (see Section 2.3.1).

First, cyclooctene was chosen as a model substrate to determine the performances at room temperature of different WO₃·H₂O/H₂O₂–H₂O/H₃PO₄/H₂SO₄/Q⁺A⁻/cyclooctene/solvent systems. Some results are given in Table 1. Under PTC conditions, the catalytic activity of the parent system without H₃PO₄ or H₂SO₄ was evaluated at room temperature (entry 1).

The dinuclear oxoperoxo and probably the mononuclear anions, $[\{WO(O_2)_2(H_2O)\}_2(\mu-O)]^{2-}$ and $[WO(O_2)_2(OH)(H_2O)]^-$, respectively, are the main species in the aqueous phase when there is no added assembling ligand in the reaction medium [18,19,36]. With an undemanding substrate such as cyclooctene, these species are usually weakly active; this is related to their hydrophilic character, as reported previously [20]. The addition of H_2SO_4 leads to higher conversions for shorter reaction times (entries 2 and 3), but still below the values obtained with the pure phosphate-based system (entry 4; 72% conversion for 1 h and 97% conversion for 2 h). For phosphate-free systems, a test performed with a greater amount of sulfuric acid (3.4 mmol instead of 0.85 mmol) shows that the same conversion can be reached only after 19 h (see Table 1, entries 2 and 3), demonstrating the need to carefully control the sulfuric acid addition. This could be explained not only by the pH change (see [18] and Section 3.5), but also by other equilibria involving Cl^- , HSO_4^- , SO_4^{2-} and oxoperoxo species and their hydrophilic character.

When both H_3PO_4 and H_2SO_4 are added to the reaction medium, a synergetic effect on the catalytic activity is observed. High conversions and selectivities are obtained in approximately 30 min (see Table 1, entry 6 and entries 3 and 4 for comparison).

In the $H_3[PW_{12}O_{40}] \cdot aq$ or $WO_3 \cdot H_2O/H_2O_2-H_2O/H_3PO_4$ systems with $[H_2O_2]/[W]/[H_3PO_4] \approx 7:1:0.75$, the ^{31}P NMR data give clear evidence for the formation of oxoperoxophosphatotungstate species: $[PWO_q]^{q-}$, $[HPO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]^{2-}$, $[PW_3O_n]^{n-}$ and $[PO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]^{3-}$, designated PW_1 , PW_2 , PW_3 and PW_4 . These complexes can be considered the active species or their precursors [14,18–20] in phosphate-based systems. According to previous work, several oxoperoxosulfato complexes can be isolated from the $WO_3 \cdot H_2O/H_2O_2-H_2O/H_2SO_4$ /onium salt/solvent [24] or $Na_2MO_4 \cdot 2H_2O$ ($M = Mo, W$)/ $H_2O_2-H_2O/[(CH_3)_4N]^+HSO_4^-$ [37,38] systems, which are polynuclear species formed from strongly acidic solutions (see Fig. 1). Thus, we suspect the in situ formation of these anions and of $[SO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]^{2-}$, which is a powerful oxidant in stoichiometric amounts but a poor catalyst for the epoxidation of alkenes [24]. It appears that both oxoperoxo-phosphato and -sulfato complexes can be responsible for the observed enhanced catalytic activity. The ^{31}P NMR results obtained on the heterometallic $[PO_4\{M_2O_2(\mu-O_2)_2(O_2)_2\}]^{3-}$ anions ($M = Mo$ and W) [35] led us to propose a competitive chemical exchange of $\{MO(O_2)_2\}$ species between phosphato complexes. Under the experimental conditions, $[PO_4]^{3-}$ is a more powerful coordinating agent than $[SO_4]^{2-}$. Results for the stoichiometric epoxidation of cyclooctene and of other monoolefins with the $[N(Bu_4)]_2[SO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]$ salt (denoted SW_2) show that half of the peroxide oxygen is transferred to the olefinic substrate. Oxoperoxosulfatotungstate is the most efficient dinuclear analogue [24]. There is evidence of initially high catalytic activity that drops due to partial breakdown of the heteropolyoxoperoxotungstate framework and the formation of less active species such as S_2W_3 . Oxygen transfer by SW_2 causes the structure of the dinuclear species to collapse at room temperature.

These data point to a possible contribution of transient oxoperoxosulfato species. This is confirmed by entries 8, 9, and 10: with the oxoperoxophosphato Arquad salt, $Q_2[HPO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]$, and with no more phosphate added, the addition of H_2SO_4 in the reaction medium enhances the catalytic activity. This may result from SW_2 and also from the fact that sulfate (formed on neutralization) is more hydrophilic [39], thus modifying the extractability into organic solvent of the oxoperoxophosphatotungstates.

3.2. Influence of solvent

For systems involving the $[PO_4]^{3-}$ assembling ligand alone (Table 1) and with toluene as the solvent, the epoxide yield (55%) is lower (entries 4 and 5) than with chloroform (72%) at 1 h of reaction time. Indeed, kinetic studies on various catalyzed reactions under PTC conditions have shown that chlorinated solvents often give better results [10]. For systems with the joint addition of $[SO_4]^{2-}$ and $[PO_4]^{3-}$ anions, the influence of the solvent is not so marked, with nearly the same activity observed for only slightly different reaction times (see entries 7 and 11). Moreover, with toluene, a synergetic effect due to addition of the $[SO_4]^{2-}$ anion is also seen (entries 5 and 11).

3.3. Influence of onium salt

To remove the chloride anion, which has a strong ion-pairing effect on the quaternary ammonium cation and can also be coordinated to the tungsten center (with a subsequent dramatic effect on reactivity), we first used $[Me(n-C_8H_{17})_3N]^+HSO_4^-$ as the phase-transfer agent. Results are collected in Table 2. Without additional phosphoric acid or sulfuric acid, the conversion is moderate (entry 1; 82% conversion for 6 h) but better than the value for entry 1, Table 1. Note that now the $[SO_4]^{2-}$ ligand is added to the medium via the phase-transfer agent. Again, even if the $[SO_4\{W_2O_2(\mu-O_2)_2(O_2)_2\}]^{2-}$ anion, in stoichiometric amounts, is a powerful oxidant for the epoxidation of alkenes, the initial catalytic activity falls off due to breakdown of SW_2 species and their rate-limiting regeneration [24]. In contrast, when phosphoric acid is added to the catalytic system, the epoxide is obtained in high yield (entry 2). The same results are obtained even if sulfuric acid is subsequently added to the reaction mixture (entry 4), indicating that the sulfate anion associated with the phase-transfer agent is sufficient to promote catalytic activity.

These results (entry 1, Table 2) demonstrate that the counterion of the quaternary ammonium goes into the organic phase and stabilizes oxoperoxosulfato complexes, which may account for the enhanced catalytic activity observed. When catalytic epoxidation is performed in toluene instead of chloroform, 94% conversion is reached after 1 h of reaction time (see entries 3, 4 and 5 in Table 2).

We studied three phase-transfer agents: methyltri-*n*-octylammonium chloride $[Me(n-C_8H_{17})_3N]^+Cl^-$, methyltri-*n*-octylammonium hydrogensulfate $[Me(n-C_8H_{17})_3N]^+HSO_4^-$, and methyltri-*n*-octylammonium dihydrogenophosphate $[Me(n-$

Table 3
Effect of phase-transfer catalyst (PTC): nature of the anionic species^a

Entry	PTC	Time (h)	Conversion ^b (selectivity) (%)
1	[CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ N] ⁺ H ₂ PO ₄ ⁻	1	55 (97) ^c
		2	80
2	[CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ N] ⁺ HSO ₄ ⁻	1	9 (25) ^c
		2	17
3	[CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ N] ⁺ Cl ⁻	1	6 (16) ^c
		2	9

^a Reaction conditions: cyclooctene (7.7 mmol), WO₃·H₂O (0.13 mmol), 30 wt% H₂O₂ (10.3 mmol); H₂O (1 mL); PTC (onium salt; 0.0975 mmol), toluene (5 mL) at 21 °C.

^b Determined by GC analysis.

^c CHCl₃ as solvent.

C₈H₁₇)₃N]⁺H₂PO₄⁻. Note that for these experiments (Table 3), no additional phosphate and/or sulfate are added. The results for the epoxidation of cyclooctene clearly demonstrate a dramatic effect of the anion; under similar reaction conditions, the conversions, selectivities and thus yields are higher with [Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻ (entry 1) than with the other two agents. The order of decreasing activity toward epoxidation of cyclooctene is [Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻ ≫ [Me(*n*-C₈H₁₇)₃N]⁺HSO₄⁻ > [Me(*n*-C₈H₁₇)₃N]⁺Cl⁻. The importance of the nature of the tungsten source is first underlined by the marked activity increase at room temperature with the catalyst system without organic solvent: WO₃·H₂O (0.032–0.13 mmol), 30 wt% H₂O₂ (30.9 mmol), H₂O (3 mL), cyclooctene (15.4 mmol), [Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻ (0.195 mmol), which displays turnover numbers as high as 110–470 per tungsten atom at 21 °C for 1.5 h (yields ≥95%). These are better than previous results [28] obtained at 90 °C with Na₂WO₄.

3.4. Epoxidation of not-too-demanding substrates

Given that [Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻ gives the best results, it was used in the following experiments. The results for the epoxidation of several alkenes without addition of phosphoric acid using the chloride-free WO₃·H₂O/H₂O₂–H₂O–H₃O⁺/[Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻/alkene/toluene system are listed in Table 4. Fair to high conversions and selectivities are obtained at room temperature, or at 60 °C for 1-octene, within 2–4 h (entries 1–3). Moreover, the system: WO₃·H₂O/H₂O₂–H₂O–H₃O⁺/[Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻/alkene/toluene can be reused without loss of activity. The results presented in Fig. 2 clearly show that the cyclooctene oxide yield remains constant even after 5 consecutive runs. With a terminal olefin such as octene-1, a yield of 74% was obtained after 4 h of reaction time. Although this is lower than the values (81–94%) obtained with Noyori's Na₂WO₄·2H₂O/H₂O₂–H₂O–H₃O⁺/NH₂CH₂PO₃H₂/[Me(*n*-C₈H₁₇)₃N]⁺HSO₄⁻/toluene system, in this work the reaction was carried out at 90 °C for 4 h [28,34,40]. Notwithstanding the fact that several other parameters, such as the Q⁺/W ratio, should be taken into account for optimization of the catalytic system [29], better catalytic activities are generally obtained when WO₃·H₂O is used instead

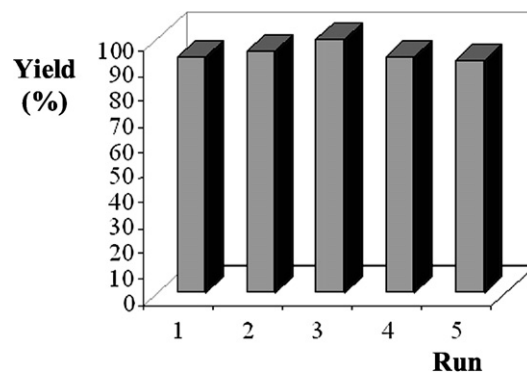



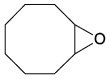

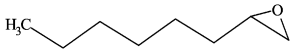
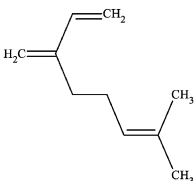
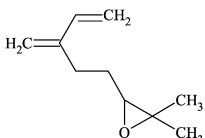
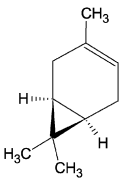
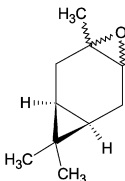
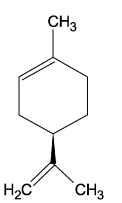
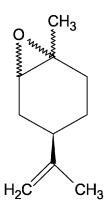
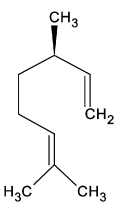
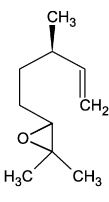
Fig. 2. Re-use of the “WO₃·H₂O/H₂O₂–H₂O–H₃O⁺/[Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻/cyclooctene/toluene” catalyst system showing no loss of activity over 5 consecutive cycles.

of Na₂WO₄·2H₂O [19]. This has been confirmed by many experiments. With Na₂WO₄·2H₂O instead of WO₃·H₂O (entry 1, Table 4), only 91% conversion is obtained after 42 h in toluene (see also Table 4, entry 1). As reported previously [29], the effect of the Q⁺/W ratio on the overall yield is also seen in this work; the respective oxide yields for Q⁺/W = 0.75 and 1.5 are 80 and 96% (see Table 3, entry 1; Table 4, entry 1).

3.5. Preparation of acid-sensitive epoxides

Several terpenes, including (*R*)-(+)-limonene, were used in this work. The epoxides are known to be acid-sensitive, leading generally to decreased selectivity (see Table 4, entries 5 and 6). However, with β-myrcene and δ³-carene, it is possible to obtain high conversion of terpene with excellent selectivity (entries 3 and 4). Buffered aqueous hydrogen peroxide solution can be used to overcome the ring opening of epoxides by water, which can be either base- or acid-catalyzed and is used extensively in the production of diols [41,42]. The commonly used buffers are generated with either sodium hydrogenocarbonate [42] (pK_a(CO₂·H₂O/HCO₃⁻) = 6.4 and pK_a(HCO₃⁻/CO₃²⁻) = 10.3) or disodium hydrogenophosphate (pK_a(H₂PO₄⁻/HPO₄²⁻) = 7.2). To compare these buffers, we choose (*R*)-(+)-limonene epoxidation with the WO₃·H₂O/H₂O₂–H₂O–H₃O⁺/[Me(*n*-C₈H₁₇)₃N]⁺H₂PO₄⁻/toluene system. The buffer precursor is added in such a way that the pH of the reaction medium is close to the pK_a of the acid–base couple, 6.4 for the carbonate buffer and 7.2 for the phosphate buffer. The possible oxidation products are given in Scheme 1. It has been shown that the acid-catalyzed ring opening of either the *cis* or *trans* isomer leads to the same (*trans*-diaxial) diols [43–45]. The same product is expected from both isomers, because the isopropenyl group anchors the ring conformation and diaxial opening predominates [45]. Because formation of this product from the *cis* isomer requires nucleophilic attack on the tertiary carbon center rather than on the secondary center, as occurs for the *trans* isomer, the *cis* isomer might be expected to open more slowly than the *trans* isomer [46]. Selectivity toward the mono-epoxides in the oxidation of limonene is controlled by the *trans/cis* ratio (1b/1a; see Scheme 1) of the epoxides, which is close to 1:1 when good selectivity is achieved [18,29,47]. Most reports in-

Table 4
Epoxidation of some olefins by two-phase system: $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / [\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^- / \text{toluene}^a$

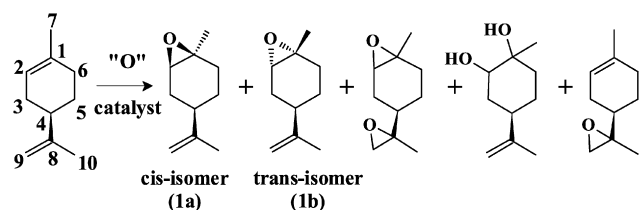
Entry	Substrate	Reaction time (h)	Product	Conversion (%) selectivity (%) yield ^b (%)
1	 cyclooctene	2		96
				100
				96
2 ^d	 1-octene	4		91
				100
				91
3	 β -myrcene	3		74
				100
				74
4	 δ^3 -carene	3		98
				100
				98
5	 (<i>R</i>)-(+)-limonene	2		85
				100
				85
6	 (+)- β -citronellene	3		95
				58
				55

^a Reaction under PTC conditions at 21 °C: olefin (7.7 mmol); $\text{WO}_3 \cdot \text{H}_2\text{O}$ (0.13 mmol), 30 wt% H_2O_2 (10.3 mmol), H_2O (1 mL), $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^-$ (0.195 mmol), toluene (5 mL).

^b Determined by GC analysis.

^c $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.13 mmol) instead of $\text{WO}_3 \cdot \text{H}_2\text{O}$.

^d Reaction carried out at 60 °C.



Scheme 1. Oxidation products of (*R*)-(+)-limonene.

dicates that generally a mixture of the mono- and di-epoxides is formed. The highly selective formation of a 1:1 mix of *trans/cis* 1,2-epoxide with a 94% conversion and 93% selectivity using a methylrhenum(V) oxide bis-picolinate precursor in the presence of 10 wt% H_2O_2 is known [47]. With (*R*)-(+)-limonene without buffer, after 2 h reaction time at room temperature, conversion is very high but selectivity is low (see Table 4, entry 5). In contrast, use of NaHCO_3 results in high selectivity, but total

Table 5
Catalytic epoxidation of (*R*)-(+)-limonene by $\text{WO}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{buffer}/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-/\text{toluene system}^a$

Test	Time (h)	<i>T</i> (°C)	Buffer precursor (mmol)		Conversion (%)	1a/1b ^b	Selectivity (%)
			NaHCO_3	$\text{Na}_2\text{HPO}_4\text{-aq}$			
1	2	21	0.64	0	0	–	–
	4				6	0.42	100
	23				42	0.81	96
	25				48	0.99	94
	27				50	1	97
	69				84	0.94	97
	73				87	1.11	98
	94				94	1.19	98
96				94	1.10	98	
2	2	21	0.52	0	32	0.61	100
	4				56	0.48	98
	13				100	0.05	≤70
3	2	21	0	0.39	20	0.45	100
	4				38	1.05	100
	18				86	1.05	99
	22				91	1.17	99
	25				94	1.21	97
	27				95	1.25	98
4	5	40	0	0.39	95	1	99

^a Reaction under PTC conditions: $\text{WO}_3 \cdot \text{H}_2\text{O}$ (0.13 mmol), 30 wt% H_2O_2 (10.3 mmol), H_2O (1 mL), $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-$ (0.195 mmol; 90.8 mg), toluene (5 mL), (*R*)-(+)-limonene (7.7 mmol).

^b See Scheme 1.

conversion of the substrate takes more than 4 days (see Table 5, test 1). In the presence of insufficient buffer, the conversions are higher but the selectivities are lower, and the **1b/1a** ratios are much less than 1 (Table 5, test 2). Thus, the NaHCO_3 buffer decreases catalytic system activity (pH and Na^+ effects).

With Na_2HPO_4 , an increase in selectivity is also observed compared with the unbuffered system (see Table 4, entry 5; Table 5, test 3). However, a reaction time of more than 1 day at room temperature is needed to quantitatively convert limonene into its mono-epoxides. Increasing the temperature from 21 to 40 °C results in improved activity (Table 5, tests 3 and 4) while selectivity remains constant. The regioselectivity was very high, and formation of limonene-8,9-epoxides was not observed. Comparing the two buffers at room temperature shows that the phosphate-based salt is more useful, because similar conversions are obtained with shorter reaction times compared with NaHCO_3 (see Table 5, tests 1 and 3). Note that the increased catalytic activity observed also can be explained by the favored formation of oxoperoxophosphato species due to the further addition of phosphate species. The phosphate can act as an assembling ligand, contrary to the carbonate anion, which can modify the concentrations of the active oxoperoxo species and even the mechanism by which the oxygen atom is transferred to the olefin [42,48].

3.6. NMR identification of active species

³¹P NMR experiments were performed to gain insight into these catalytic systems and to evaluate the role of the qua-

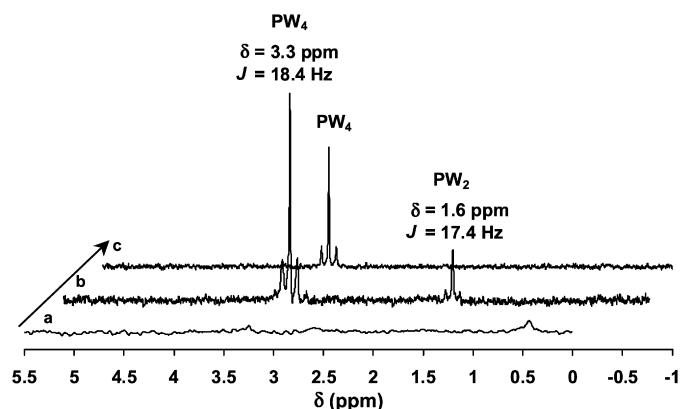


Fig. 3. ³¹P NMR spectra of catalyst systems (organic phase, see Section 2.4 for experimental details): (a) $\text{WO}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{H}_3\text{PO}_4/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{Cl}^-/\text{CHCl}_3 \approx 1:17:0.25:1:0.05$ (424 scans), (b) $\text{WO}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{H}_3\text{PO}_4/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-/\text{CHCl}_3 \approx 1:17:0.25:1:0.05$ (120 scans), (c) $\text{WO}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{H}_3\text{PO}_4/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{HSO}_4^-/\text{CHCl}_3 \approx 1:17:0.25:1:0.05$ (64 scans).

ternary onium salt on the different oxoperoxo species. Under our conditions, methyltri-*n*-octylammonium chloride (Aliquat®) does not efficiently extract the oxoperoxophosphato species from the aqueous phase. A very weak signal related to phosphate-containing species can be detected in the organic phase (Fig. 3a); this is correlated with poor catalytic activity (Table 3, entry 3). This result can be explained by the strong ion-pairing effect between chloride and $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+$, disfavoring formation and migration into the organic phase of other pairs that are catalytically active [18]. With systems involving $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-$ or $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{HSO}_4^-$ transfer agents, known species are easily identified by ³¹P NMR of the organic phases. For the $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-$ salt (see Fig. 3b), the signal at 3.3 ppm (² $J_{\text{W-P}} = 18.4$ Hz) corresponds to the $[\text{PO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{3-}$ anion (designated PW_4) and the other at 1.6 ppm (² $J_{\text{W-P}} = 17.4$ Hz) to the $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ anion (designated PW_2). Given that the coupling constants ² $J_{\text{W-P}}$ and the chemical shifts $\delta(^{31}\text{P})$ depend on several factors, including solvent effects, protonation of the $\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$ moieties, and counteranion effects, the ion-pairing effect (see Fig. 4) may be operative. The attributions can be made unambiguously based on integration of the satellites with respect to the central line and of the coupling constants [18,19]. These complexes are very active for the epoxidation of alkenes under stoichiometric or catalytic conditions [14,18–20,29]. Note that the PW_1 and PW_3 complexes cannot be detected in the organic phase (Fig. 3b; $\text{W/P} = 0.8$). We tentatively explain this result based on the fact that the mononuclear and trinuclear complexes are nonsymmetric and do not have a strong ion-pairing effect with $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+$, and they have an H_2O ligand lying on the apical position, which is normally occupied by one of the oxygen of the bridging peroxy group (see, e.g., the crystal structures of $[\text{NMe}_4]_2[(\text{PhPO}_3)\{\text{MO}(\text{O}_2)_2\}_2\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}]$, $\text{M} = \text{Mo}, \text{W}$ [49]). This results in increased hydrophilicity and thus lower solubility in organic phases of the PW_1 and PW_3 complexes

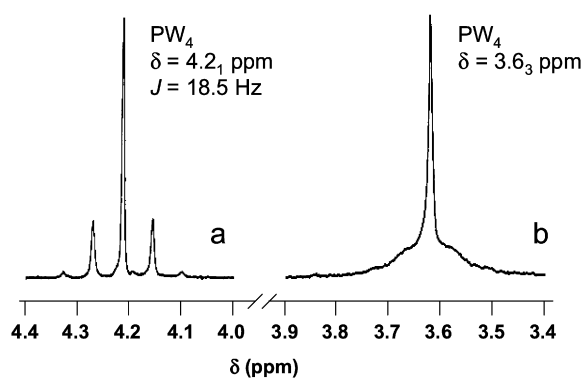


Fig. 4. An illustration of the ion-pairing effect. (a) ^{31}P NMR spectra of a $\text{CH}_3\text{CN}/\text{CDCl}_3$ (90/10 v/v) solution of $(\text{Bu}_4\text{N})_3[(\text{PO}_4)\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O})_2\}_2]$ with well-resolved satellites (60 scans). (b) CDCl_3 solution of $\{[(\text{C}_{18}\text{H}_{37})_3\text{N}^+](\text{C}_{16}\text{H}_{33})_2(\text{C}_2\text{H}_5)_2\}_3[(\text{PO}_4)\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O})_2\}_2]$ (300 scans). The ^{31}P line is flanked by broad unresolved humps (this salt of the Arquad cation is insoluble in CH_3CN).

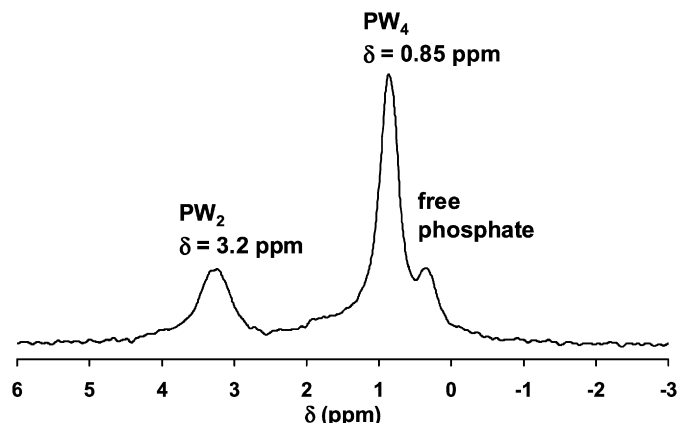


Fig. 5. ^{31}P NMR spectra (aqueous phase, see Section 2.4 for experimental details) of the system: $\text{WO}_3\cdot\text{H}_2\text{O}/\text{H}_2\text{O}_2/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-/\text{CHCl}_3 \approx 1:21:0.75:0.03$ (56 scans); pH 1.5–2.0.

compared with PW_2 and PW_4 . With $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{HSO}_4^-$ (Fig. 3c), the introduction of HSO_4^- as a counteranion of $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]^+$ modifies the ^{31}P spectrum dramatically; only PW_4 remains in the organic phase. Unfortunately, sulfur NMR cannot be used to monitor oxoperoxosulfato species; nevertheless, the $[\text{SO}_4\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O})_2\}_2]^{2-}$ (SW_2) anion may account for the synergetic effect of the addition of sulfate to the catalytic system (see Table 2, entry 1; Table 3, entry 2) and the better transfer of the PW_4 anionic species.

The ^{31}P NMR spectrum of the aqueous phase (Fig. 5) is not well resolved, due to the formation of bubbles during the experiment. This may be due to H_2O_2 and/or peroxo ligand decomposition; exchange processes between anionic species associated with H_3O^+ and Q^+ also can contribute, as can an ion-pairing effect [18,35]. The data unambiguously show the formation of oxoperoxophosphato tungsten species [18] which are tentatively attributed to PW_n species ($n = 2; 4$) even if the formation of anionic species PW_1 and PW_3 cannot be excluded.

NMR experiments also were conducted on systems without a preliminary addition of phosphate to the reaction medium; that is, phosphate addition is achieved only through the in-

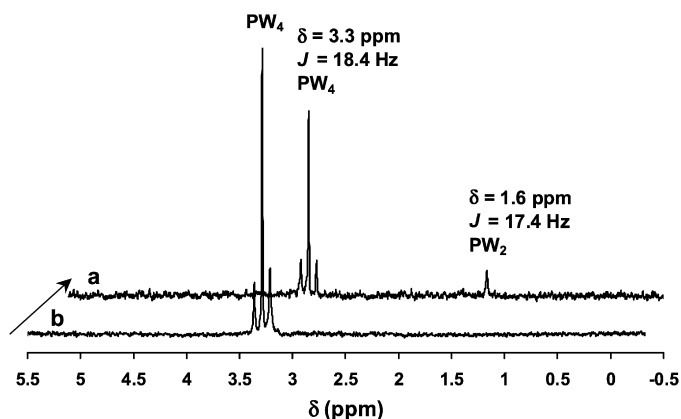


Fig. 6. ^{31}P NMR spectra of catalyst systems (organic phase, see Section 2.4 for experimental details): (a) $\text{WO}_3\cdot\text{H}_2\text{O}/\text{H}_2\text{O}_2/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-/\text{CHCl}_3 \approx 1:17:1:0.05$ (104 scans), (b) $\text{WO}_3\cdot\text{H}_2\text{O}/\text{H}_2\text{O}_2/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-/\text{H}_2\text{SO}_4/\text{CHCl}_3 \approx 1:17:1:4.7:0.05$ (104 scans).

roduction of onium salt. The ^{31}P NMR spectrum (Fig. 6a) is similar to that of the $\text{WO}_3\cdot\text{H}_2\text{O}/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{H}_3\text{PO}_4/[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-/\text{CHCl}_3$ system, again showing signals related to the PW_4 and PW_2 species. The addition of sulfuric acid leads to the disappearance of the signal attributed to the PW_2 anion (Fig. 6b; cf. Fig. 3c). Moreover, no free phosphate or phosphoric acid is detected in the organic phase. Thus, all of the phosphato groups are bonded to tungsten atoms to give active species that can enter into the catalytic cycle. Based on recent dynamic studies [35], it can be concluded that the PW_4 and PW_2 species are certainly in chemical exchange; however, there is no direct chemical exchange between free phosphate and oxoperoxophosphatotungstate. The situation is unclear with sulfato species, although some are transferred to the organic phase, as evidenced by chemical analysis.

4. Conclusions

This work studied the effect of adding phosphate and/or sulfate species on the activity toward olefin epoxidation in phase-transfer catalysis systems with Arquad 2HT® (counteranion: Cl^-). A synergy is observed due to the combined effect of the phosphate and sulfate anions compared with systems involving either ligand alone. For phosphate-free systems, the addition of sulfuric acid should be carefully controlled, because it can lead to decreased catalytic performance.

Given that the nature of the phase-transfer agent may have a dramatic influence on catalytic performance, this study considered three phase-transfer agents: $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{Cl}^-$, $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{HSO}_4^-$, and the $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{N}]^+\text{H}_2\text{PO}_4^-$ salts. The tests demonstrate that the latter is the best for the catalytic epoxidation of cyclooctene at room temperature using 30 wt% hydrogen peroxide as oxidant. These results are correlated with the ^{31}P NMR data. The nature of the phosphate-containing tungsten oxoperoxo species in the organic phase depends on that of the counterion of the onium group. The $[\text{PO}_4\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O})_2\}_2]^{3-}$ and $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O})_2\}_2]^{2-}$ complexes are identified with H_2PO_4^- , whereas only the former is present with H_2PO_4^- and

HSO_4^- . The importance of the tungsten(VI) source stressed previously [18,19,22–26,29] is highlighted once again by the strong activity increase at room temperature when using $\text{WO}_3 \cdot \text{H}_2\text{O}$ instead of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

Moreover, using the $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / [\text{CH}_3 - (n - \text{C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^- / \text{toluene}$ catalysis system, the preparation of not-too-sensitive epoxides can be carried out with good selectivity at room temperature. For acid-sensitive epoxides, comparing the effects of such buffers as $\text{CO}_2 \cdot \text{H}_2\text{O} / \text{HCO}_3^-$ or $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ showed that the latter appears to be superior in terms of conversion and selectivity, due in part to the phosphate ion's ability to act as an assembling ligand, in contrast to the carbonate anion. It was demonstrated that the $\text{WO}_3 \cdot \text{H}_2\text{O} / \text{H}_2\text{O}_2 - \text{H}_2\text{O} - \text{H}_3\text{O}^+ / [\text{CH}_3 - (n - \text{C}_8\text{H}_{17})_3\text{N}]^+ \text{H}_2\text{PO}_4^- / \text{cyclooctene} / \text{toluene}$ catalysis system can be reused in 5 consecutive runs with no loss in activity. To reach long lifetimes of the oxoperoxo-metal systems, these tungsten-based systems, active at 20–40 °C, can compete in terms of yields and selectivities for the synthesis of very sensitive epoxides with the $\text{CH}_3\text{ReO}_3 / \text{H}_2\text{O}_2 - \text{H}_2\text{O} / \text{Brönsted bases} / \text{organic solvent two-phase reagents}$ [47, 50]. Thus, with (*R*)-(+)-limonene, the primary oxidation products are limonene-1,2-epoxides, with a very high regioselectivity, because formation of limonene-8,9-epoxides is not observed. Moreover, the highly selective formation of a 1:1 mixture of *trans/cis*-1,2-epoxides is obtained with tungsten(VI)- or rhenium(VII)-based systems (this work and [47]). The former are quite complex and interesting from equilibrium and dynamic standpoints; further kinetic studies are needed to explore the detailed mechanisms in these systems. The active species must have an appropriate partition coefficient, one that allows it to interact with both the organic medium and the aqueous oxidant for regeneration. We now have a reliable approach to choosing the ideal alkyl ammonium salt that avoids the need for trial-and-error experiments. Further applications of this catalytic system to other oxidations are under investigation.

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References

- [1] J.-P. Schirmann, S.Y. Delavarenne, *Hydrogen Peroxide in Organic Chemistry*, EDI, Paris, 1979, p. 21.
- [2] G. Strukul (Ed.), *Catalytic Oxidation with Hydrogen Peroxide as Oxidant*, Kluwer, Dordrecht, 1992, p. 1.
- [3] C.W. Jones, *Applications of Hydrogen Peroxide and Derivatives*, Roy. Soc. Chem., Cambridge, 1999.
- [4] W.R. Sanderson, *Pure Appl. Chem.* 72 (2000) 1289.
- [5] W.R. Sanderson, in: J. Clark, D. Macquarie (Eds.), *Handbook of Green Chemistry and Technology*, Blackwell Publishing, Oxford, 2002, p. 258, and references therein.
- [6] G. Sienel, R. Rieth, K.T. Rowbottom, *Ullmann's Encyclopedia of Industrial Chemistry*, sixth ed., Verlag Chemie, Weinheim, 2003, p. 269.
- [7] J.T. Lutz, in: H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg (Eds.), *Kirk–Othmer Encyclopedia of Chemical Technology*, fourth ed., Wiley, New York, 1994.
- [8] G.B. Payne, P.H. Williams, *J. Org. Chem.* 24 (1959) 54.
- [9] W.P. Weber, G.W. Gokel, in: *Phase Transfer Catalysis in Organic Synthesis, Reactivity and Structure*, vol. 4, Springer, Berlin, 1977.
- [10] E.V. Dehmlow, S.S. Dehmlow, in: *Phase Transfer for Catalysis*, second ed., *Monographs in Modern Chemistry*, vol. 11, Verlag Chemie, Weinheim, 1983.
- [11] H.H. Freedman, *Pure Appl. Chem.* 58 (1986) 857.
- [12] C.M. Starks, C.L. Liotta, M. Halpern, *Phase-Transfer Catalysis: Fundamentals, Applications, and Industrial Perspectives*, Chapman & Hall, New York, 1994.
- [13] Y. Sasson, G. Rothenberg, in: J. Clark, D. Macquarie (Eds.), *Handbook of Green Chemistry and Technology*, Blackwell Publishing, Oxford, 2002, p. 206, and references therein.
- [14] J.-M. Brégeault, *Dalton Trans.* (2003) 3289, and references therein.
- [15] C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* 48 (1983) 3831.
- [16] Y. Matoba, H. Inoue, J. Akagi, T. Okabayashi, Y. Ishii, M. Ogawa, *Synth. Commun.* 14 (1984) 865.
- [17] S. Sakaguchi, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* 61 (1996) 5307.
- [18] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Brégeault, *Inorg. Chem.* 33 (1994) 871.
- [19] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, *Inorg. Chem.* 30 (1991) 4409.
- [20] J.-M. Brégeault, M. Vennat, L. Salles, J.-Y. Piquemal, Y. Mahha, E. Briot, P.C. Bakala, A. Atlamsani, R. Thouvenot, *J. Mol. Catal. A Chem.* 250 (2006) 177.
- [21] C. Venturello, R. D'Aloisio, J.C.J. Bart, M. Ricci, *J. Mol. Catal.* 32 (1985) 107.
- [22] J.-Y. Piquemal, L. Salles, G. Chottard, P. Herson, C. Ahcine, J.-M. Brégeault, *Eur. J. Inorg. Chem.* (2006) 939.
- [23] J.-Y. Piquemal, L. Salles, C. Bois, F. Robert, J.-M. Brégeault, *C. R. Acad. Sci. Ser. IIB Chim.* 319 (1994) 1481.
- [24] L. Salles, F. Robert, V. Semmer, Y. Jeannin, J.-M. Brégeault, *Bull. Soc. Chim. Fr.* 133 (1996) 319.
- [25] J.-Y. Piquemal, C. Bois, J.-M. Brégeault, *Chem. Commun.* (1997) 473.
- [26] J.-Y. Piquemal, S. Halut, J.-M. Brégeault, *Angew. Chem., Int. Ed. Eng.* 37 (1998) 1146.
- [27] L. Salles, J.-Y. Piquemal, M. Gentil, Y. Mahha, P. Herson, J.-M. Brégeault, *Polyhedron*, submitted for publication.
- [28] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella, R. Noyori, *Bull. Chem. Soc. Jpn.* 70 (1997) 905.
- [29] J.-M. Brégeault, R. Thouvenot, S. Zoughebi, L. Salles, A. Atlamsani, E. Duprey, C. Aubry, F. Robert, G. Chottard, *Stud. Surf. Sci. Catal.* 82 (1994) 571; J.-M. Brégeault, R. Thouvenot, S. Zoughebi, L. Salles, A. Atlamsani, E. Duprey, C. Aubry, F. Robert, G. Chottard, *Proceedings of the Second World Congress and Fourth European Workshop Meeting*, 20–24 September 1993, Benalmádena, Spain, 1993.
- [30] T. Rüther, W.R. Jackson, A.M. Bond, *Aust. J. Chem.* 55 (2002) 691.
- [31] J. Gao, Y. Chen, B. Han, Z. Feng, C. Li, N. Zhou, S. Gao, Z. Xi, *J. Mol. Catal. A Chem.* 210 (2004) 197.
- [32] M.-L. Wang, T.-H. Huang, *J. Chem. Eng. Jpn.* 36 (2003) 231.
- [33] M.-L. Wang, T.-H. Huang, W.-T. Wu, *Chem. Eng. Commun.* 191 (2004) 27.
- [34] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem.* 61 (1996) 8310.
- [35] L. Salles, R. Thouvenot, J.-M. Brégeault, *Dalton Trans.* (2004) 904.
- [36] J. Prandi, H.B. Kagan, H. Mimoun, *Tetrahedron Lett.* 27 (1986) 2617.
- [37] M. Hashimoto, H. Ichida, Y. Sasaki, *J. Coord. Chem.* 37 (1996) 349.
- [38] M. Hashimoto, T. Iwamoto, H. Ichida, Y. Sasaki, *Polyhedron* 10 (1991) 649.

- [39] E.V. Dehmlow, B. Vehre, W. Broda, *Synthesis* (1985) 508.
- [40] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* (2003) 1977.
- [41] M.C.A. Van Vliet, I.W.C.E. Arends, R.A. Sheldon, *Synlett* (2001) 248.
- [42] B.S. Lane, M. Vogt, V.J. DeRose, K. Burgess, *J. Am. Chem. Soc.* 124 (2002) 11946.
- [43] H. Schmidt, *Suomen Kemistilehti B* 31 (1958) 61.
- [44] R. Wylde, J.-M. Teulon, *Bull. Soc. Chim. Fr.* (1970) 758.
- [45] E.E. Royals, J.C. Leffingwell, *J. Org. Chem.* 31 (1966) 1937.
- [46] L. Salles, A.F. Nixon, N.C. Russell, R. Clarke, P. Pogorzelec, D.J. Cole-Hamilton, *Tetrahedron: Asymmetry* 10 (1999) 1471.
- [47] A. Deloffre, S. Halut, L. Salles, J.-M. Brégeault, J.R. Gregorio, B. Denise, H. Rudler, *J. Chem. Soc. Dalton Trans.* (1999) 2897, and references therein.
- [48] N. Gharah, S. Chakraborty, A.K. Mukherjee, R. Bhattacharyya, *Chem. Commun.* (2004) 2630.
- [49] W.P. Griffith, B.C. Parkin, A.J.P. White, D.J. Williams, *J. Chem. Soc. Dalton Trans.* (1995) 3131.
- [50] F.E. Kühn, R.W. Fischer, W.A. Herrmann, in: M. Beller, C. Bolm (Eds.), *Transition Metals for Organic Synthesis*, second ed., Wiley-VCH, Weinheim, 2004, p. 357, and references therein.